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(54) MANUFACTURE OF FRP COMPOSITES

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(57) **ABSTRACT**

Techniques are provided for producing low-cost FRP composites which contain heavy tow fibres. Techniques are provided for uniform impregnation and efficient bonding of these heavy tow fibres which eliminates “racetracking,” thus resulting in cost-effective and well performing FRP composites.

Figure 1

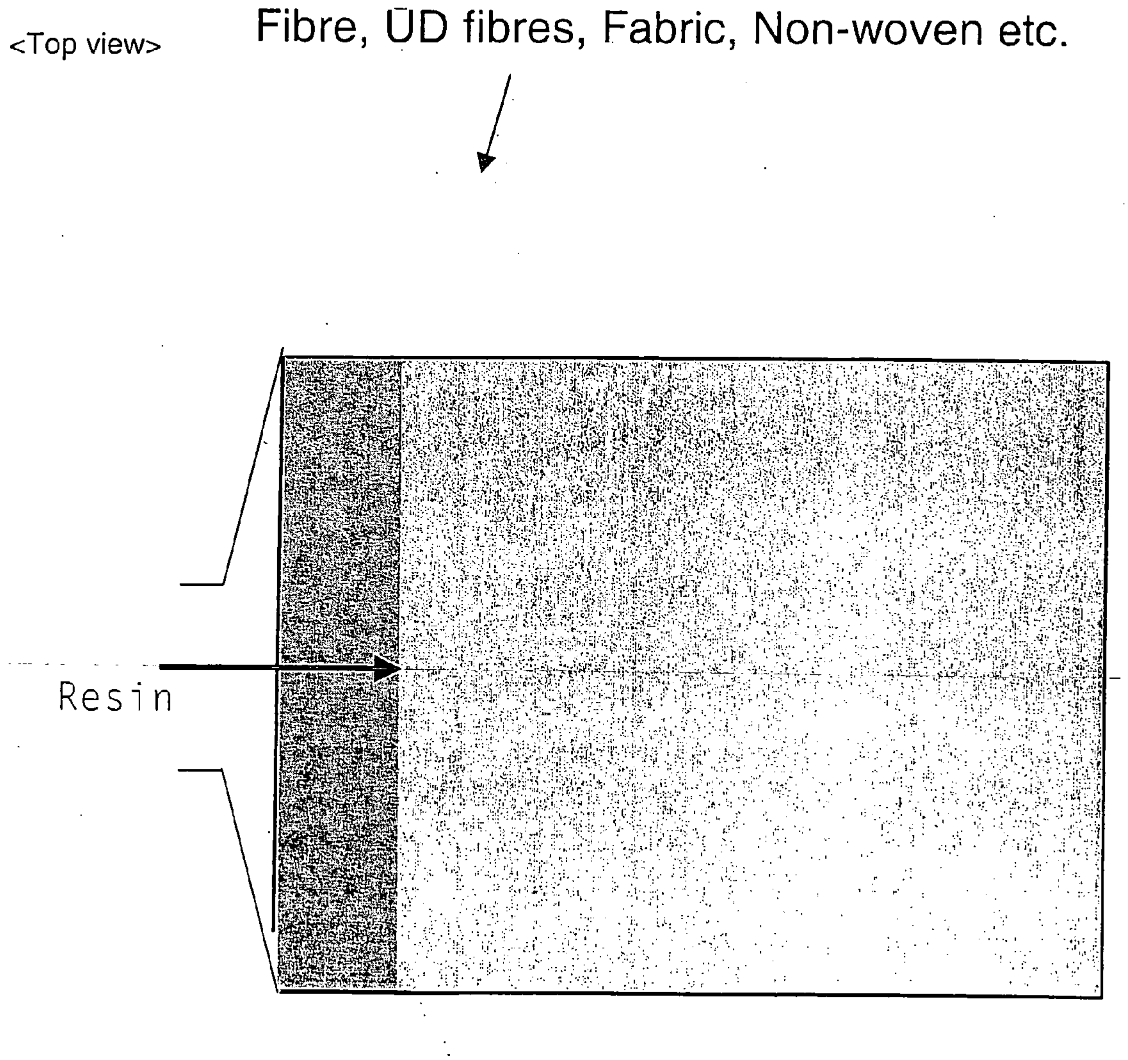


Figure 2

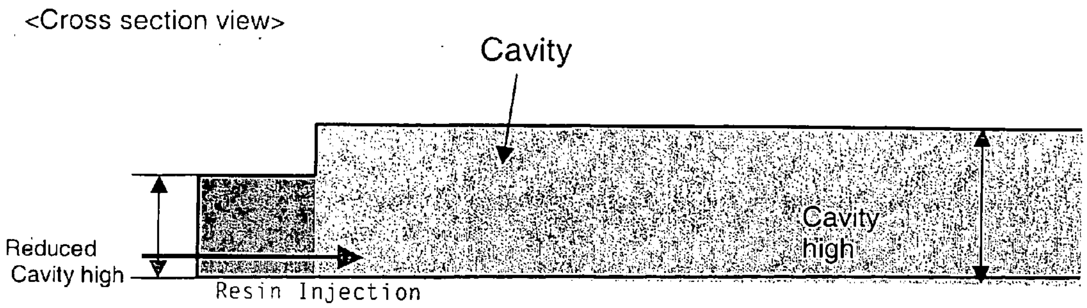


Figure 3

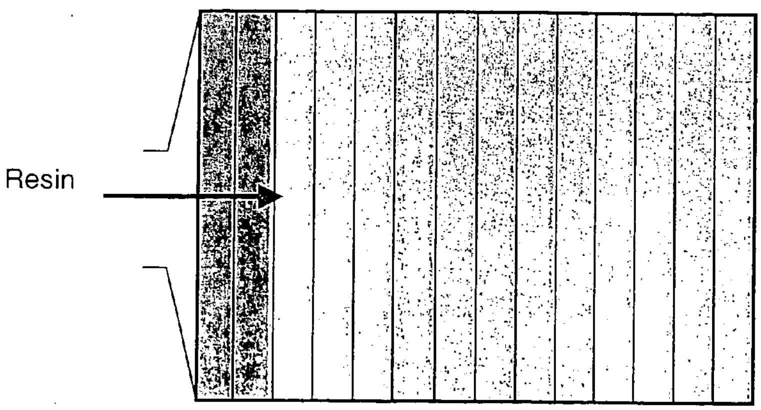


Figure 4a

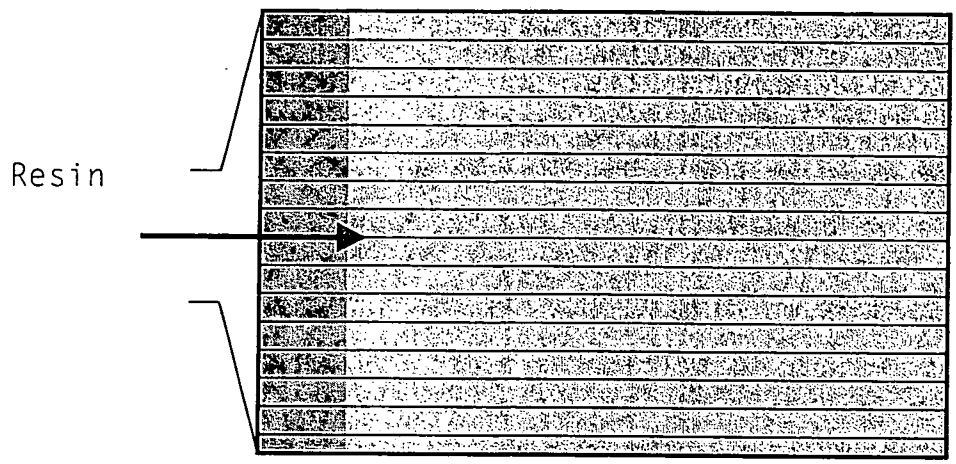


Figure 4b

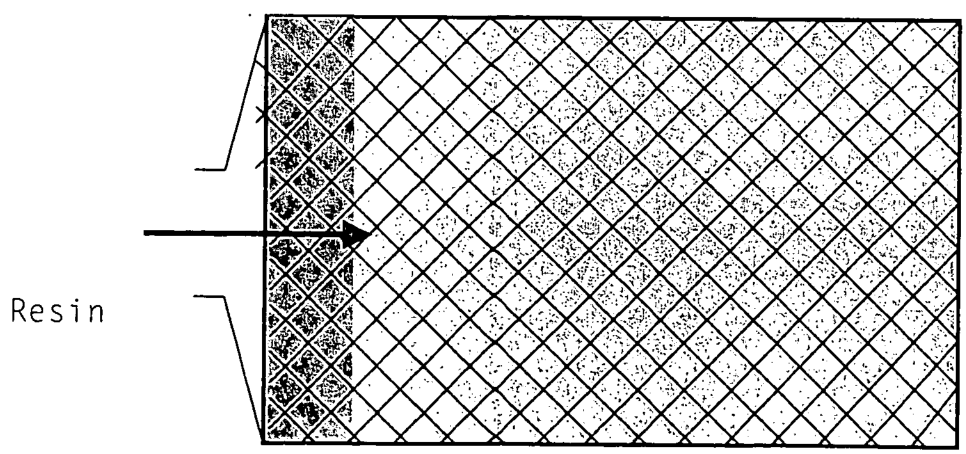
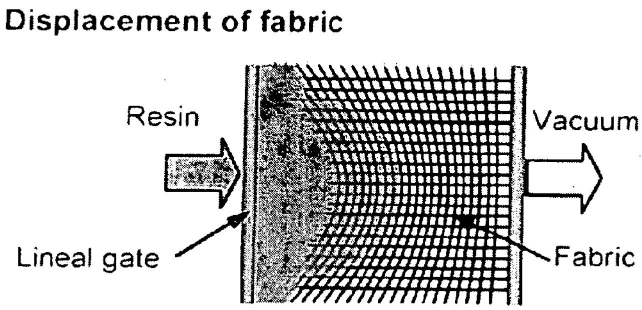


Figure 5



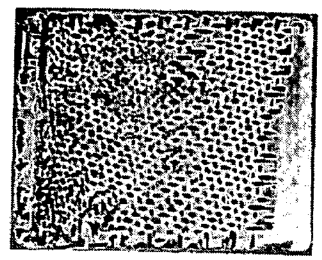
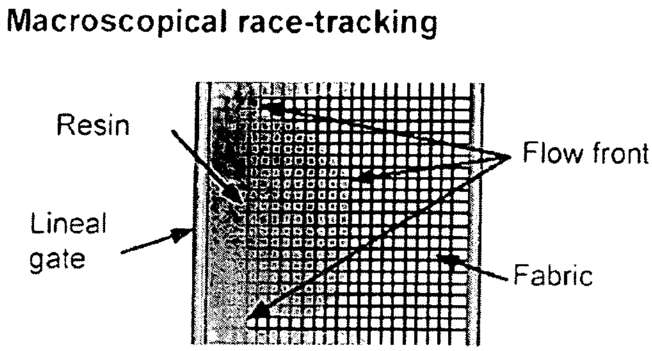


Figure 6


Macroscopical race-tracking
Resin
Flow front
Lineal gate
Fabric

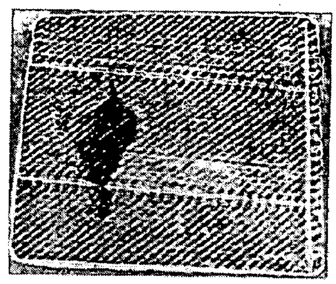
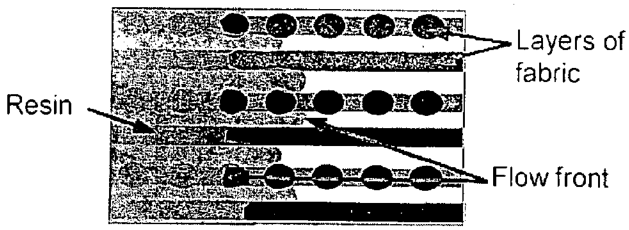


Figure 7

Interlaminar race tracking



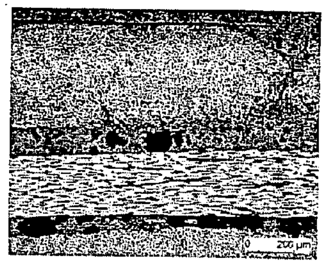


Figure 8

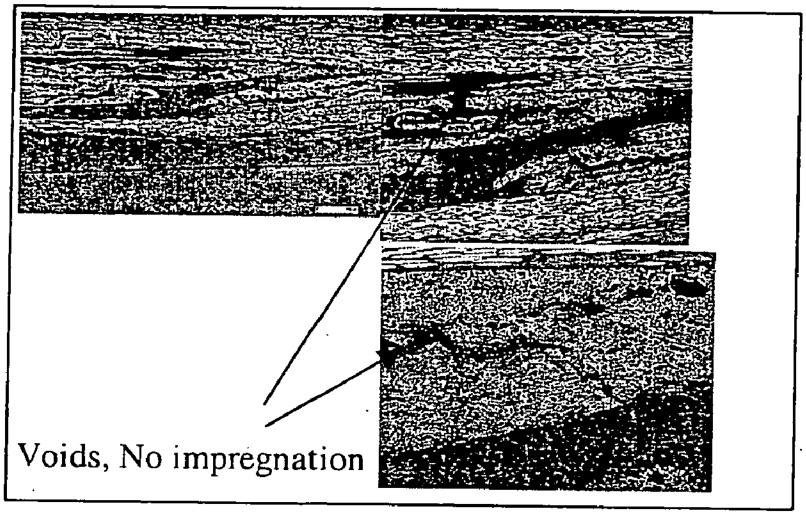


Figure 9

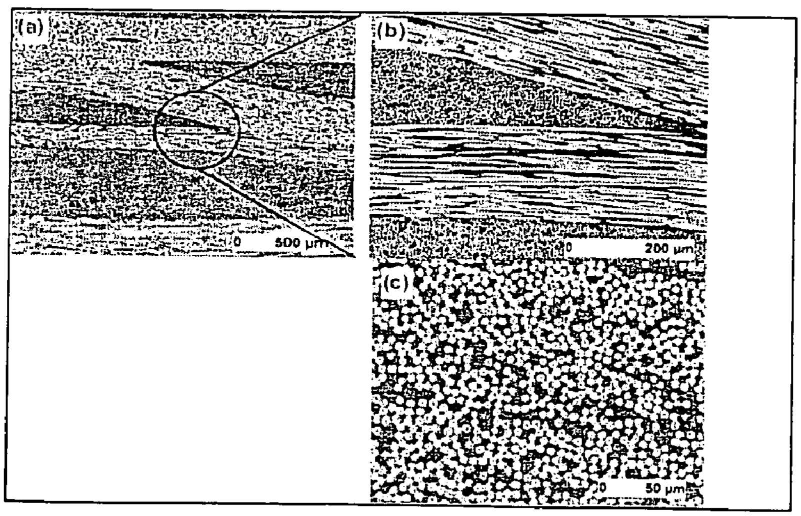
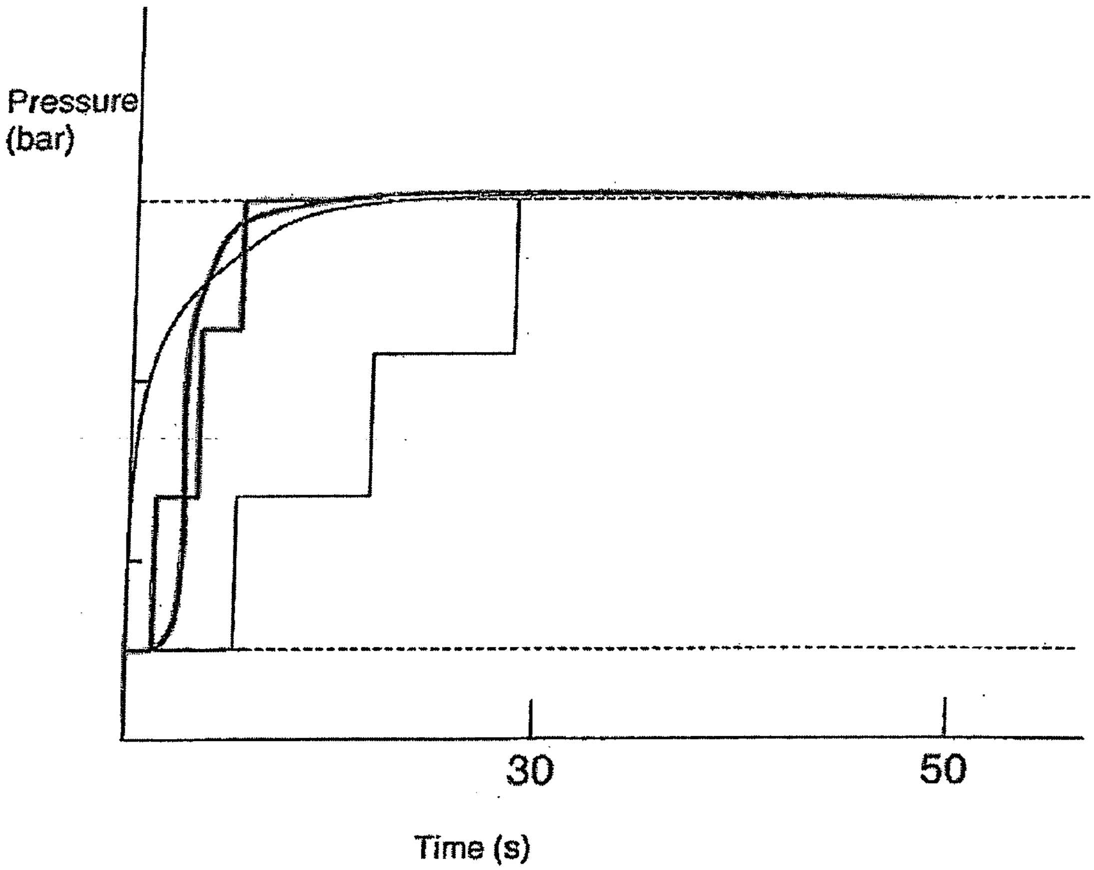


Figure 10

Different pressure ramps



MANUFACTURE OF FRP COMPOSITES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is related to and claims priority from European Patent Application No. 05 002 047.8 filed on Feb. 1, 2005, which is incorporated by reference herein in its entirety.

FIELD OF THE INVENTION

[0002] The present invention relates to manufacture of fibre-reinforced plastics (FRP) composites.

BACKGROUND OF THE INVENTION

[0003] Composite materials and in particular CFRP (carbon fibre reinforced plastics) composite materials are characterized by their low weight, great strength and high stiffness in comparison with traditional materials such as wood, steel, aluminum etc. For these reasons, they are used in a number of applications ranging from the aerospace, construction, automotive industries to the sports and medical fields.

[0004] In the 1970s, for instance, sporting good manufacturers started making use of CFRP composites in the manufacture of fishing rods, golf clubs, and tennis rackets. In the 1990s, commercial plane manufacturers such as Boeing and Airbus started adopting CFRP composites for primary and secondary structural parts in order to reduce the weight of planes and have highly performing flying machines. Nowadays, because of their high strength and light weight, these CFRPs can be used for the reinforcement of structures and their use is expanding to the building and civil engineering field. The medical field also makes use of the composites for X-ray inspection equipment and even for artificial limbs. In yet another example application, the performance of CFRP composites is contributing to the reduction of weight of housing electronic tools and equipment such as laptops, LCD projectors, cameras etc.

[0005] One sector where the use of composite materials is constantly evolving is the automotive industry. Conventionally, CFRP composites have been used for racing cars. However, as a result of increasing attention to environmental problems, there is a tendency to try to use these composites for commercial, mass-produced cars. Indeed, composite materials offer great potential in reducing vehicle weight, thus increasing fuel efficiency and reducing CO_2 emissions.

[0006] Conventional FRP manufacturing processes include pultrusion or resin moulding processes. The conventional Resin Transfer Moulding (RTM) process is used for making composite parts and is capable of satisfying the low-cost/high-volume 500-50,000 parts per year of the automotive industry as well as the higher performance/lower volume 50-5,000 parts per year of the aerospace industry.

[0007] In the resin transfer moulding process, a two-part, matched-metal mould (or tool) is made. A preform is placed into the mould, and the mould is closed. A resin is then pumped under low pressure through injection ports into the mould. Both the mould and resin can be heated as needed for the application.

[0008] Conventionally, both thermoplastic and thermoset resins are used to produce composite materials. However, for structural applications, thermoplastic resins have conventionally lacked the mechanical properties of thermoset resins. Mainly, poor fibre impregnation and lack of fibre adhesion cause this performance gap. Thermoplastic resin conventionally used in the manufacture of CFRP composites starts off with a high viscosity, typically 100-1000 Pa·s, and thus impregnation becomes a difficult task. On the other hand, thermoplastic resins offer the advantage that they can be recycled and in an environmental context, this becomes important.

[0009] Low viscosity thermoplastic resins have recently been developed. U.S. Pat. No. 6,673,872, which is incorporated by reference herein in its entirety, describes the addition of a polyarylene ether having a low intrinsic viscosity to high performance, amorphous thermoplastic polymers providing improved melt flow properties to such polymers without causing degradation of important mechanical properties such as impact strength and ductility.

[0010] With RTM, one may be capable of making complex and quality composite parts with short cycle times. However, by introducing more complexity into the part, one also introduces higher probability of disturbances, such as racetracking of resin during impregnation along the preform edges. Racetracking is a phenomenon whereby a resin travels more quickly along a mould edge due to the lower fibre volume fraction in this region providing less resistance to flow. With severe racetracking, the exiting resin can bypass some of the fibres and produce dry spots within the composite. This results in poor quality FRP composites.

[0011] Another possible disturbance is the displacement of the fibres during the RTM process. For example, if the matrix viscosity is too low and the timescales long, shaping pressures may cause the resin to be squeezed out of the laminate. Alternatively, too high a viscosity coupled with a short duration can result in the fibres being unable to adjust to the flow pattern and distortion can ensue.

[0012] These disturbances are a function of the fabric type, resin type, preform manufacturing method, the placement of fibres and the fibre distribution in the cavity mould. Their impact on the behavior of the FRP component is of high importance and their elimination is thus vital for high performance applications.

[0013] An endeavor towards eliminating racetracking is described in U.S. Pat. No. 6,406,660, which is incorporated by reference herein in its entirety. U.S. Pat. No. 6,406,660 purports to describe a vacuum bag method for the manufacture of CFRP, which attempts to prevent "racetracking" by cutting the fabrics to a particular pattern and supporting the cover plate in a slightly different manner. Resin with a viscosity less than 500 mPa*s may be used.

[0014] The introduction of high performance FRP components in a structure however significantly depends on the raw material and the manufacturing process costs. Conventionally, the cost of FRP containing materials has been very high and often prohibitive for the general consumer. Therefore, significant endeavor to reduce the cost of such manufacturing process has been a high priority for manufacturers. For instance, JP 2003-020542, which is incorporated by reference herein in its entirety, describes a process for the manufacture of CFRP composites from carbon fibre fabric for use as aircraft structural members, wherein the cost of the process is reduced by the use of less expensive carbon fibres of moderate tow (12K to 24K).

[0015] While Resin Transfer Moulding is a conventional method for mass production of composites, there still remains a need for the manufacture of improved FRP composites by elimination of racetracking defects, reduction of fabric displacement when using pressure injection systems and reduction of the manufacturing process costs.

SUMMARY OF THE INVENTION

[0016] One embodiment of the present invention provides a process for manufacturing a fibre-reinforced plastics (FRP) composite and to a device for carrying out such process. One embodiment of the present invention relates to a heavy tow (thick bundle) FRP-composite free of "dry spots", a process for manufacturing such composite by preventing "racetracking," and a device for carrying out such process. In one embodiment, the present invention advantageously provides for the manufacture of low cost FRP composites which exhibit good performance.

[0017] In view of the problems described in the background section and the need for cost reduction and process improvement, one embodiment of the invention provides a process for producing low-cost FRP composites which contain heavy tow fibres, and a method for uniform impregnation and efficient bonding of these heavy tow fibres which eliminates "racetracking", thus resulting in cost-effective and well performing FRP composites.

[0018] One embodiment of the present invention is described herein with reference to carbon fibres. It will be readily apparent to one having ordinary skill in the art, however, that the present invention is also applicable to the use of other fibre reinforced plastic composites. For example, the process described herein can also be applied to the manufacture of glass-fibre reinforced plastics wherein the glass fibres are used as thick bundles.

[0019] One embodiment of the present invention provides a process for the manufacture of carbon-fibre reinforced plastic (CFRP) composites, the process comprising impregnation of heavy tow carbon fibres with low viscosity resin. The carbon fibres used in the process may be combined with other types of fibres, for example glass fibres.

[0020] One embodiment of the present invention uses fibres having a tow equal or greater than 24000 filaments. The fibres used in the process according to one embodiment of the present invention may be in the form of woven fabric sheets with interlacing points which may further be laminated and multi-compacted. In one embodiment, the volume content of the fibres in the fabric sheets is less than 60%. In another embodiment, the volume content of the fibres in the fabric sheet is less than 30%.

[0021] According to one embodiment of the present invention, a resin used to impregnate the fibres has a low viscosity. In one embodiment, impregnation of fibres by resin can be carried out by injection of the resin into the fabric sheet. Injection of the resin into the fibre may be made at any site in the fabric area, wherein the pressure difference between the injection side and the downstream side of the resin flow may be increased stepwise.

[0022] In one embodiment, the flow direction of the resin may be against gravity and is not perpendicular to the fibre orientation. Further, the fabric sheet can be clamped at the edges of a mould before resin injection.

[0023] According to one embodiment of the present invention, edges of the mould wherein the fabric sheet is placed have a reduced cavity high. In one embodiment, the fibre volume fraction at the reduced cavity high is no more than 55%. In another embodiment, the fibre volume fraction at the reduced cavity high is no more than 50%.

[0024] One embodiment of the present invention provides a process for the manufacture of carbon-fibre reinforced plastic (CFRP) composites by impregnation of carbon fibres with resin from an injection side towards a downstream side, the pressure on the injection side being incremented stepwise.

[0025] A further embodiment of the present invention provides for CFRP composite manufactured by the processes described above. One embodiment of the present invention yields a CFRP composite wherein the volume content of fibres is less than 60%. Another embodiment of the present invention yields a CFRP composite wherein the volume content of fibres is less than 30%.

[0026] One embodiment of the present invention provides for the use of heavy tow carbon fibres with low viscosity resin for the manufacture of CFRP composite. A further embodiment of the present invention provides for the manufacture of such composites, comprising a mould with reduced cavity high at the edges wherein the fibres or fibre fabric is placed, a clamping mechanism to prevent fibres or fibre fabric displacement, and a pressure ramp injection system for injecting the resin into the fabric under stepwise increments of pressure. The resin can be injected directly into the fibre or fibre fabric.

[0027] One embodiment of the present invention provides a device for manufacturing CFRP composites according to the processes described above.

DESCRIPTION OF THE DRAWINGS

[0028] **FIG. 1** shows a top view of a mould displaying a resin injection inlet according to one embodiment of the present invention.

[0029] **FIG. 2** shows a cross sectional view of a mould with a reduced cavity high on the resin injection side, according to one embodiment of the present invention.

[0030] **FIG. 3** shows a top view of a mould wherein the fibres are perpendicular to the resin flow, according to one embodiment of the present invention.

[0031] **FIG. 4*a*** shows a top view of a mould wherein the fibres are parallel to the resin flow, according to one embodiment of the present invention.

[0032] **FIG. 4*b*** shows a top view of a mould wherein the fibres are arranged so as not to be perpendicular to the resin flow, according to one embodiment of the present invention.

[0033] **FIG. 5** shows a top view of a mould wherein fibres are displaced due to a resin high flow rate:

[0034] **FIG. 6** shows a top view of a mould wherein macroscopical racetracking of the resin occurs.

[0035] **FIG. 7** shows a cross sectional view of interlaminar racetracking in between the fabric layers.

[0036] **FIG. 8** shows a view of heavy tow impregnated carbon fibres obtained using convention technology.

[0037] **FIG. 9** shows a view of heavy tow impregnated carbon fibres obtained according to one embodiment of the present invention.

[0038] **FIG. 10** shows a graph of pressure versus time, displaying different pressure ramps used according to one embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0039] One embodiment of the present invention provides a process for the manufacture of fibre reinforced plastics (FRP) composites, comprising impregnation of fibres with resin.

[0040] One embodiment of the present invention is described herein with reference to carbon fibre reinforced plastics (CFRP). However, one skilled in the art will recognize that that embodiments of the invention may also be used for the manufacture of other fibre reinforced plastics such as glass fibre reinforced plastics (GFRP).

[0041] Carbon fibres, also referred to as graphite fibres, can be industrially produced from polyacrylonitrile fibre or pitch. According to one embodiment of the present invention, oxidation of these starting materials followed by carbonizing/graphitizing stages yield carbon fibre filaments which can then be grouped to form tows.

[0042] One embodiment of the present invention uses heavy tow fibres or fibre tows comprising at least 24000 filaments.

[0043] Fibres can be assembled in many different ways that are suitable for application in one embodiment of the present invention. For example, unidirectional arrangements such as tapes, strips, fabrics or even single tow can be used. In one embodiment, the fibre can be used as twisted yarn, untwisted yarn or non-twisted yarn.

[0044] According to one embodiment of the present invention, the tows can be weaved into a cloth with interlacing points. The woven fabric (in the form of mats, knitted fabrics etc.) may be, for example, balanced or multiaxial. Example styles of weaving can be a plain weave, a twill weave or a satin weave.

[0045] According to one embodiment of the present invention, in addition to carbon fibres, inorganic fibres such as glass fibres, alumina fibres, or silicon nitride fibres, or organic fibres such as aramid fibres or nylon may be used. For example, these fibres may be long fibres, short fibres, woven fabric, a mattress, or a combination of these, and may be orderly or disorderly arranged in the carbon fibres. In one embodiment, glass fibres are used in addition to carbon fibres.

[0046] Example resins for application in the present invention are thermosetting resins such as epoxy resins and vinyl ester resins, or thermoplastic resins such as nylon, polycarbonate and also monomers or oligomers which react to be polymers etc.

[0047] According to one embodiment of the present invention, a thermoplastic resin is used, wherein the term "thermoplastic resin" includes those polymers that soften when exposed to heat and then return to original condition when cooled to room temperature. Examples of thermoplastic resins include ABS (acrylonitrile, butadiene and styrene) resin, acrylic/PMMA (polymethylmethacrilate) resin, ethylene tetrafluoroethylene resin, EVA (ethylene vinyl acetate) resin, HDPE (high density polyethylene) resin, LDPE (low density polyethylene) resin, LLDPE (linear low density polyethylene) resin, Masterbatch resin, nylon, perfluoroalkoxy resin, polyacetal resin, polyamide resin, polybutylene terephthalate resin, polycarbonate resin, polyetheretherketone resin, polyetherimide resin, polyethersulfone resin, polyethylene terephthalate resin, polyimide resin, polyphenylene oxide resin, polypropylene (homopolymer and copolymer) resin, polysulfone resin, polystyrene (crystal and impact) resin, polyurethane resin, polyvinyl chloride resin.

[0048] Advantages of thermoplastics over thermosets include long shelf life, good toughness and the fact that processing is concerned with physical transformations only. There is no chemistry involved and therefore extended cure cycles are not necessary. As a consequence there is potential for rapid, low cost fabrication with simplified quality control procedures.

[0049] According to one embodiment of the present invention, the resin used features a low viscosity at the time of impregnation. In one embodiment, the viscosity of the resin to be injected is less than 50 mPa·s.

[0050] According to one embodiment of the present invention, sheets of woven fabric comprising the fibres described above are cut into a particular shape suitable for incorporation to the mould to obtain a fibre woven fabric base material for forming a CFRP composite. In one embodiment, the shape of the preform can be cut accurately so as to fit perfectly into the mould and thus avoid macroscopical racetracking of the resin as is depicted in **FIG. 6**.

[0051] According to one embodiment of the present invention, the number of sheets to be stacked can be: selected according to the structure or appearance desired for the composite. In one embodiment, where several sheets are used, the laminate can be multicompacted so as to provide a homogeneous fibre area. Compaction of the lay-up can be carried out by the application of a temporary vacuum bag and vacuum to remove trapped air, wherein repetition of such compaction provides a homogeneous fibre area that can be impregnated with the low viscosity resin according to one embodiment of the present invention.

[0052] According to one embodiment of the present invention, the fabric sheet is then clamped to the mould in a way described below, the mould is closed, heat is applied and the resin is injected under pressure.

[0053] The use of low viscosity resin in the impregnation process of the present invention can result in a high flow rate. Such high flow rate can also be increased by the application of pressure and can result in fabric displacement. The following techniques can be used to avoid fabric displacement caused by high flow rate of the resin.

[0054] According to one embodiment of the present invention, the fibre fabric is clamped to the mould. The edges of the tool can be lower than the cavity high as shown in **FIG. 2**. Further, in one embodiment, the fibre volume content at the edges is less than 55%. In a further embodiment, the fibre volume content at the edges is less than 50%.

[0055] According to one embodiment of the present invention, the fibre fabric is placed in the mould in such an orientation that the carbon fibres are not perpendicular to the resin flow as shown in **FIGS. 4***a* and **4***b*. A perpendicular orientation of the fibres with respect to the resin flow, such as that depicted in **FIG. 3**, would result in the fabric displacement depicted in **FIG. 5**. In that respect, one embodiment of the present invention uses weaved fabric with interlacing points.

[0056] According to one embodiment of the present invention, it is possible that the fibre volume content of the laminate be less than 30%. A lower fibre volume content than that used in conventional manufacturing methods (30%-60%) usually results in a non uniform distribution of the fibre in the cavity. For example, the fibre volume content inside the fibre bundles themselves can be high, whereas the fibre volume content can be low in between the different fabric layers. In conventional manufacturing methods, the lower fibre volume content will result in interlaminar race-tracking (i.e. faster resin flow, even with relatively high viscosity resin) as shown in **FIG. 7** and thus a worse impregnation of the fibres ensues. One embodiment of the present invention therefore uses very low viscosity resin in order to improve the impregnation of the fibres even when a high flow rate is used.

[0057] According to one embodiment of the present invention, in order to further optimize impregnation of the fibres, the resin can be injected directly in the fabric. According to a further embodiment, the pressure applied for the resin injection can be incremented stepwise so as to allow the flow front of the resin to become balanced before the next pressure increment, thus resulting in better impregnation, as shown in **FIG. 10**. For example, the resin may be injected anywhere from 15 psi to 250 psi.

[0058] According to one embodiment of the present invention, once the fabric sheet is fully impregnated, resin solidifies and the CFRP composite can be demoulded. The resulting CFRP composites are free of "dry spots" as shown in **FIG. 9**. In comparison, fibres impregnated according to conventional methods are shown in **FIG. 8**.

[0059] According to one embodiment of the present invention, finishing operations are minimal due to the near net shape of the component and the good surface finish supplied by the mould.

[0060] According to one embodiment of the present invention, a manufacturing device used to carry out the process described above can be a two-part mould with an inlet for the injection of the resin as shown in **FIG. 1**, the mould having a reduced cavity high at the edges as shown in **FIG. 2**. The process of the present invention carried out using such a manufacturing device advantageously results in high quality low cost CFRP composites.

[0061] The present invention may be embodied in various forms and should not be construed as limited to the embodiments set forth herein. Rather, these embodiments are provided so that disclosure will be thorough and will fully convey the invention to those skilled in the art. For example, while one embodiment of the invention has been described with reference to carbon fibres, one skilled in the art will recognize that other types of fibres, for example glass fibres, can be used. While particular embodiments and applications of the present invention have been illustrated and described herein, it is to be understood that the invention is not limited to the precise construction and components disclosed herein and that various modifications, changes, and variations may be made in the arrangement, operation, and details of the methods and apparatuses of the present invention without department from the spirit and scope of the invention as it is defined in the appended claims.

What is claimed is:

1. A method of manufacturing fibre reinforced plastics (FRP) composites, comprising:

impregnation of heavy tow fibres with a low viscosity resin.

2. The method of claim 1, wherein the fibres comprise one of:

carbon fibres; and

glass fibres.

3. The method of claim 2, wherein the carbon fibres are combined with at least one other type of fibres.

4. The method of claim 3, wherein the at least one other type of fibres comprise glass fibres.

5. The method of claim 1, wherein a tow of the fibres is equal to or greater than 24000 filaments.

6. The method of claim 1, wherein the fibres are woven into fabric sheets with interlacing points.

7. The method of claim 6, wherein the fabric sheets are multi-compacted.

8. The method of claim 6, wherein a volume content of the fibres in the fabric sheets is less than 60%.

9. The method of claim 6, wherein a volume content of the fibres in the fabric sheets is less than 30%.

10. The method of claim 1, wherein the resin, at a time of impregnation, has a viscosity less than 50 mPa*s.

11. The method of claim 10, wherein the resin is a thermoplastic resin.

12. The method of claim 1, wherein the impregnation is carried out by injection of the resin into a fabric sheet comprising the fibres.

13. The method of claim 12, wherein an injection point of the resin is directly in the fabric area.

14. The method of claim 12, wherein the resin is injected with stepwise increments of pressure such that a pressure at a flow front of the resin is balanced before a pressure increment.

15. The method of claim 12, wherein a flow front of the injected resin is against gravity.

16. The method of claim 12, wherein a flow direction of the injected resin is not perpendicular to an orientation of the fibres.

17. The method of claim 12, wherein the fabric is clamped at edges of a mould before the resin injection.

18. The method of claim 17, wherein the edges of the mould have a reduced cavity high.

19. The method of claim 18, wherein a fibre volume fraction at the reduced cavity high is no more than 55%.

20. The method of claim 18, wherein a fibre volume fraction at the reduced cavity high is no more than 50%.

21. A FRP composite product obtained by performing the method of claim 1.

22. The FRP composite product of claim 21, wherein a volume content of the fibres in the composite is less than 60%.

23. The FRP composite product of claim 21, wherein a volume content of the fibres in the composite is less than 30%.

24. An apparatus for the manufacture of FRP by performing the method of claim 1.

25. A method of manufacturing fibre reinforced plastics (FRP) composites, comprising:

impregnation of fibres with resin from an injection side towards a downstream side, wherein a pressure on the injection side is incremented stepwise.

26. The method of claim 25, wherein a time interval in between a first pressure increment and a second pressure increment is such that a pressure at a flow front is balanced across the downstream side before the second pressure increment.

27. The method of claim 25, wherein the fibres comprise one of:

carbon fibres; and

glass fibres.

28. An apparatus for manufacturing FRP composites, comprising:

a reduced cavity high at edges of a mould wherein fibres or fibre fabric is placed;

a clamping mechanism to prevent displacement of the fibres or the fibre fabric; and

a pressure ramp injection system, wherein a resin is injected into the mould under stepwise increments of pressure.

29. The apparatus of claim 28, wherein the resin is injected directly into the fibres or the fibre fabric under the stepwise increments of pressure.

* * * * *